

# **In-Situ Chemical Oxidation (ISCO): Case Studies and Technology Advancements**

**Battelle**

**Washington State University**

# Presentation Overview



## • Introduction

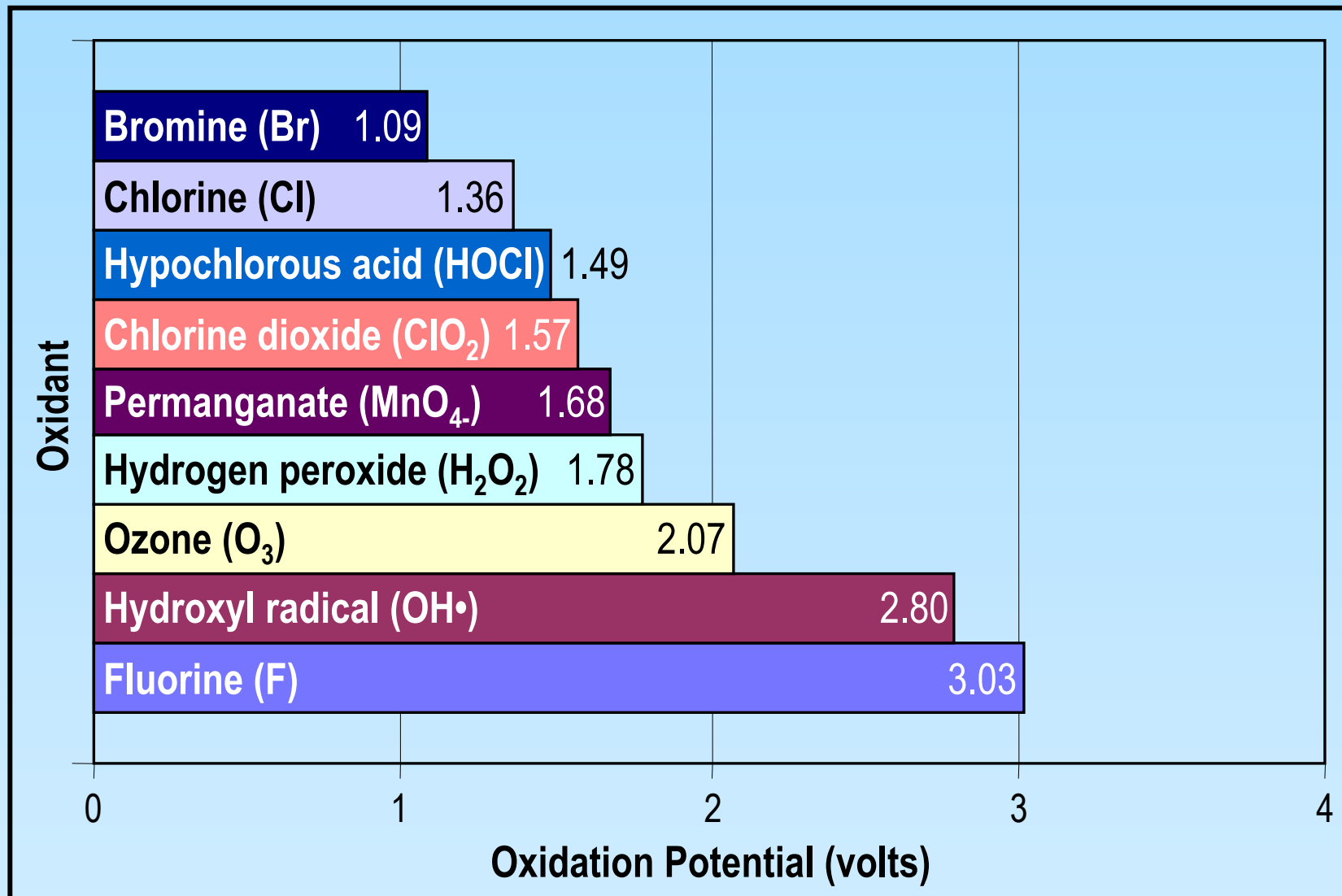
- **Advances in Understanding Permanganate Application**
  - Oxidation Chemistry and Application
  - Case Study and Cost
- **Advances in Understanding Fenton's Reagent Application**
  - Oxidation Chemistry and Application
  - Case Study and Cost
- **Conclusions**
  - Permanganate Oxidation
  - Fenton's Reagent
  - Oxidant Selection
  - Regulatory Concerns

# Principles of Common Oxidation Processes



- An oxidant is a chemical that has a tendency to accept electrons from other chemicals (preferably target contaminants in groundwater and soil)
  - The target contaminant is oxidized (loses electrons) and is transformed to a non-toxic or less-toxic product
  - Oxidation potential is a measure of the oxidative power of an oxidant. The higher the oxidation potential (volts), the greater the oxidative power.
- Permanganate ( $\text{MnO}_4^-$ ) and Fenton's reagent ( $\text{H}_2\text{O}_2$  and  $\text{Fe}_{2+}$ ) have been the most commonly used for in-situ chemical oxidation

# Oxidation Potential of Select Oxidants



# Presumed Advantages and Limitations of ISCO



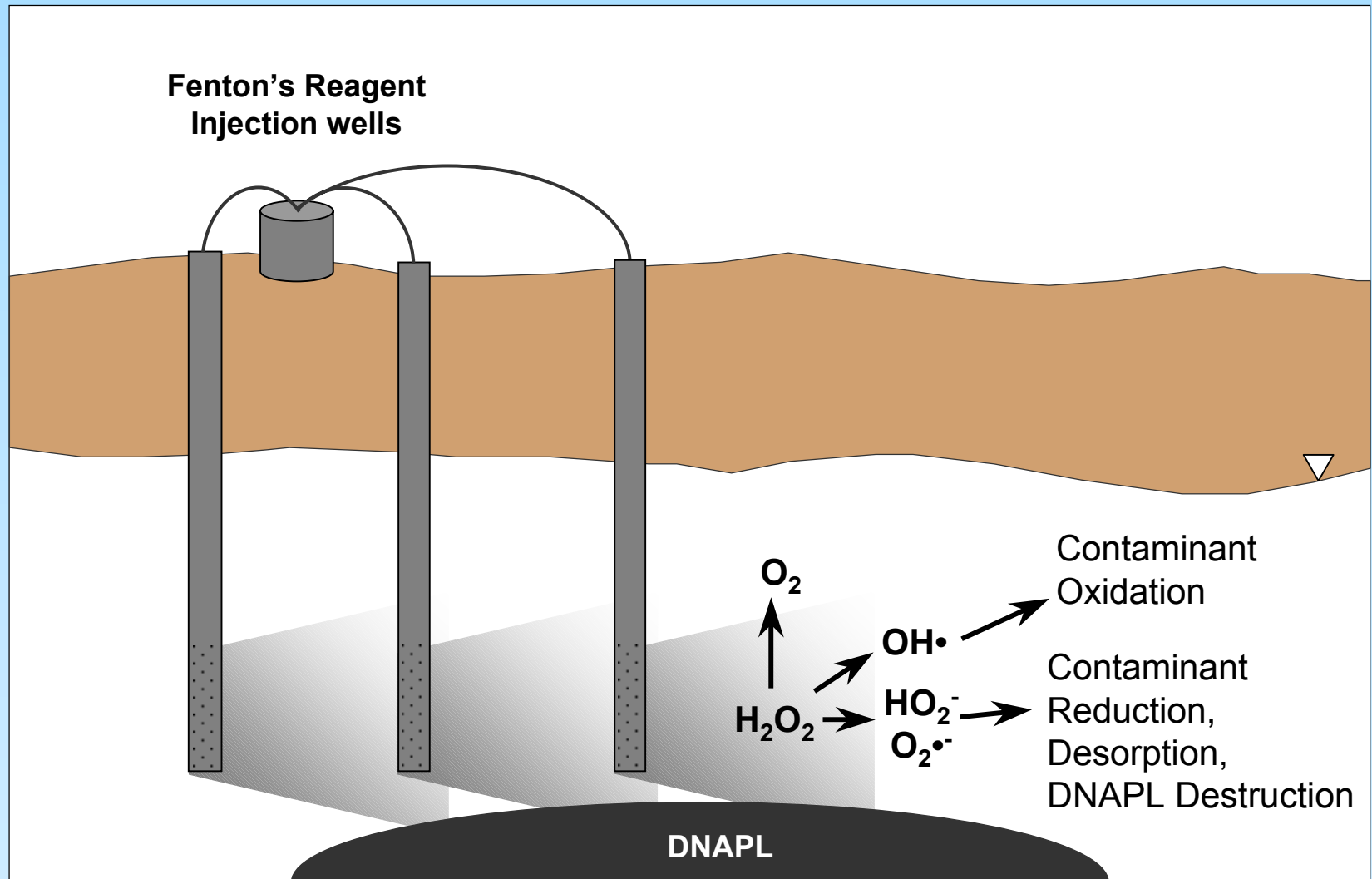
## • Presumed Advantages

- Contaminants can potentially be destroyed in situ, unlike thermal or surfactant flushing technologies
- Relatively inexpensive reagents (e.g., potassium permanganate at \$1 to \$1.50/lb) can be used
- Potentially effective with many different types of organic contaminants in sorbed and DNAPL states
- Cost-effective treatment for contaminant source zones or "hot spots"

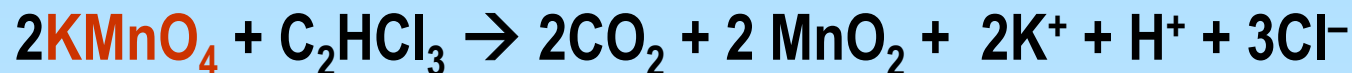
## • Apparent Disadvantages

- Some handling hazard (e.g., hydrogen peroxide)
- As with any in-situ technology, reagent delivery to the target regions may be challenging
- Strong oxidants may oxidize other (naturally occurring) reduced species in the subsurface
- An injection permit is required
- May not be cost-effective for treating very dispersed, dilute contamination (i.e., dispersed contaminant plume)

# Simplified Illustration of In-Situ Chemical Oxidation



- Permanganate oxidation



- Fenton's Reagent



# Key Questions for the Technology



- Which contaminants are treatable by ISCO?
- What determines the oxidant dosage?
- How effective is the treatment? Why do contaminant levels often rebound following ISCO?
- How do strong oxidants affect the natural aquifer media?
- If ISCO does not destroy all the target contamination, is the treated aquifer amenable to subsequent biodegradation of the residual contamination?
- What limits the effectiveness of an ISCO application?
- How do we select the best oxidant for a given site?



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# Oxidation Chemistry – Target Contaminants



- **Permanganate has been shown to oxidize:**
  - Chloroethenes (e.g., TCE)
  - PAHs
  - Chlorinated pesticides (e.g., aldrin and dieldrin)
  - High explosives
  - Some chlorophenols
- **Permanganate is ineffective with:**
  - Chlorinated alkanes (e.g., TCA, dichloroethane)
  - Aromatic hydrocarbons (e.g., benzene and chlorobenzene)
- **MTBE – is oxidized to TBA**
  - Functional group is oxidized, but not the parent structure

- Permanganate oxidation – Several researchers have documented second order kinetics
  - Rate of reaction of  $\text{MnO}_4^-$  with the COC depends on the aqueous concentration of both the  $\text{MnO}_4^-$  and the COC
- Implication
  - **Increasing** the concentration of injected  $\text{MnO}_4^-$ , increases the rate of oxidation of the COC, as well as the consumption of  $\text{MnO}_4^-$
  - Rate of  $\text{MnO}_2$  (solid) formation around injection point may increase with increasing concentration of injected permanganate solution.  $\text{MnO}_2$  solids are initially colloidal (transportable), but subsequently may coagulate.

# At very **low** concentrations, permanganate action may be too slow



Half Lives of Chloroethenes in Water		
KMnO <sub>4</sub> (mg/L)	TCE (min)	1,2-DCE (min)
1000	2.8	–
750	3.6	–
700	3	1.8
500	4.9	2.8
300	8.6	4.3
250	11.5	–
20	122	114
15	122	158
10	217	None
5	347	None

Source: Marvin et al., 2002

# Factors Affecting Permanganate Application

## – Soil Oxidation Demand



- Soil oxidation demand (SOD) often exceeds the oxidant demand of the COC, sometimes by 2 or 3 orders of magnitude
  - Multiple aquifer species contribute to SOD, including:
    - Reduced solid species (e.g., sulfides, ferrous iron minerals, etc.)
    - Natural organic matter
    - Aqueous species (dissolved iron, etc.)

# Factors Affecting Permanganate Application

## – Oxidant Dosage



- Some oxidation of these reduced native species is **desirable**
  - Surprisingly, at many sites, groundwater TOC, COD, and BOD have been found to increase, following ISCO. Complex organic matter breaks down to simpler carbon compounds that are more bioavailable.
- Completely oxidizing these native reduced species may be **undesirable**
  - If site is overdosed with permanganate, then entire redox buffering capacity of the treatment zone could be destroyed, making it difficult for anaerobic microbial populations to reestablish

# Factors Affecting Permanganate Application

## – Potential for Mobilization of Metals



- Redox-sensitive metals (e.g., Cr, As, Se, Hg) in soil could be **mobilized**
  - E.g.,  $\text{Cr}_6^+$  is more soluble (mobile) than  $\text{Cr}_3^+$
  - USGS reports average background chromium concentrations in soils across the U.S. are approximately 50 mg/kg. Background concentrations are typically as high as 100 mg/kg along the California coast
- Mobilized metals often **attenuate** in the aquifer
  - $\text{MnO}_2$  solids (naturally occurring, as well as formed by ISCO) can naturally attenuate Cr through sorption and ion exchange
  - Subsequent return to reducing conditions may cause  $\text{Cr}_6^+$  to reprecipitate as  $\text{Cr}_3^+$  (dissolved chromium may not go far)

# Factors Affecting Permanganate Application

## – Quality of $\text{KMnO}_4$



- Industrial grade  $\text{KMnO}_4$  (and to some extent  $\text{NaMnO}_4$ ) contains **Cr** as a trace impurity. However, increase in Cr in groundwater at ISCO sites has typically been more than that attributable to injected oxidant.
- Industrial  $\text{KMnO}_4$ , also contains **nickel**, which has been found at elevated levels at some sites
- Perhaps **thallium**



# Factors Affecting Permanganate Application

## – Effects on Soil Permeability



- In some aquifers, addition of permanganate has been found to reduce permeability. Paradoxically, in other aquifers permeability may actually increase.
- Factors that **reduce** permeability
  - $\text{MnO}_2$  solids formation and accumulation (affected by injected  $\text{KMnO}_4$  concentration, injection rate, and natural geochemical variables)
  - Formation of  $\text{CO}_2$  gas (depends on the carbonate composition of the aquifer and geology)
- Factors that may **increase** soil permeability include relatively high levels of oxidizable matter, such as total organic carbon, DNAPL, and reduced mineral species

# Factors Affecting Permanganate Application

## – Effect of Changes in Soil Properties



- **Post-ISCO**, COC concentrations may decrease and then increase again, even though considerable DNAPL mass has been destroyed
  - Increased permeability following ISCO may lead to increased advection and diffusion of COCs from the pores into the bulk flow
  - Oxidation of soil organic matter (to which, considerable COC may be sorbed) may cause COCs to be released into the dissolved phase
- Implication: A second injection (or multiple injections) may be desirable after a new equilibrium is reached

# Factors Affecting Permanganate Application

## – Oxidant Distribution/Process Engineering



- **Recirculation approach (injection-extraction)**
  - Better hydraulic control – better distribution of oxidant, less chance of COC migration
  - Reinjection may need to meet stricter guidelines
  - More elaborate aboveground equipment required to filter out  $\text{MnO}_2$ , replenish oxidant, and perhaps remove trace metals from recirculating water

# Factors Affecting Permanganate Application

## – Oxidant Distribution/Process Engineering (Cont.)



- **Injection Only** (currently more practiced, viewed as "easy")
  - Injection wells have to be arranged in a way that makes use of natural gradient to distribute the oxidant
  - Or, use multiple temporary injection points to inject the oxidant in several locations and depths in the target treatment zone
  - Higher injection pressures may be required in tighter soils; possibility of spreading the COCs
  - Mn (discoloration) and trace metals could migrate downgradient

# Case Study: Interagency DNAPL Consortium (IDC) Project DOE, U.S. EPA, Air Force/Navy, NASA

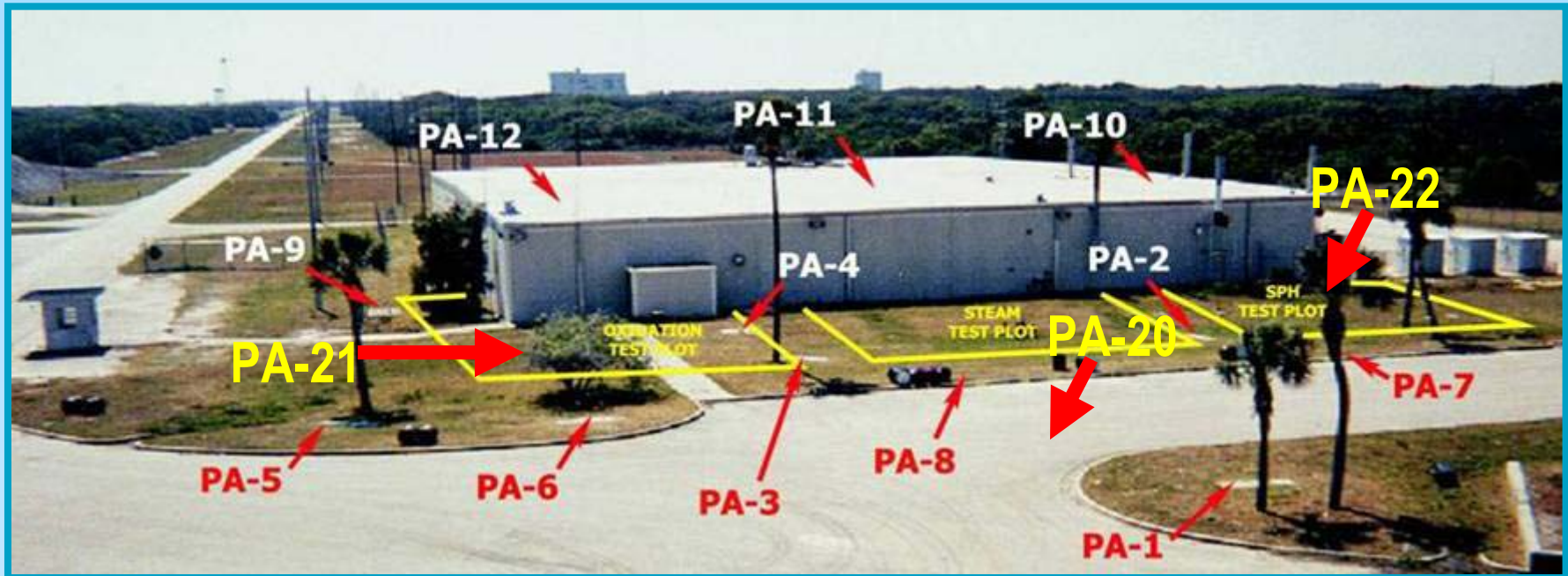


**Launch Complex 34,  
Cape Canaveral Air Force Station, FL**

Source: Battelle, 2002



# Launch Complex 34 DNAPL Site



## •DNAPL source characterization and in situ treatment

- *Six-Phase Heating*
- *Chemical Oxidation*
- *Steam Injection*

# Performance Evaluation Strategy and Goals – Cape Canaveral Air Station



- Overall goal – Meet Florida State-mandated maximum contaminant level (MCL) targets in DNAPL Source Area: 3  $\mu\text{g/L}$  TCE, 70  $\mu\text{g/L}$  DCE, and 1  $\mu\text{g/L}$  vinyl chloride
- Goal for Remediation Vendors – Remove 90% of initial DNAPL mass
- Performance Assessment Methodology
  - Are CVOCs being destroyed or recovered?
  - Is DNAPL migrating to surrounding regions?
  - Are all the CVOCs removed from the test plot being captured aboveground?
  - What is the state of the test plot after treatment? Are conditions conducive for continued biodegradation of the residual CVOCs?

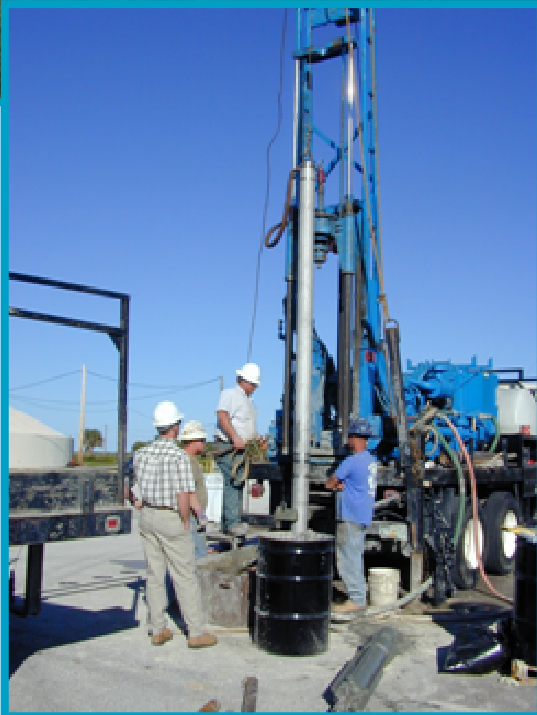
# Cape Canaveral Remediation

## –Validation of Performance



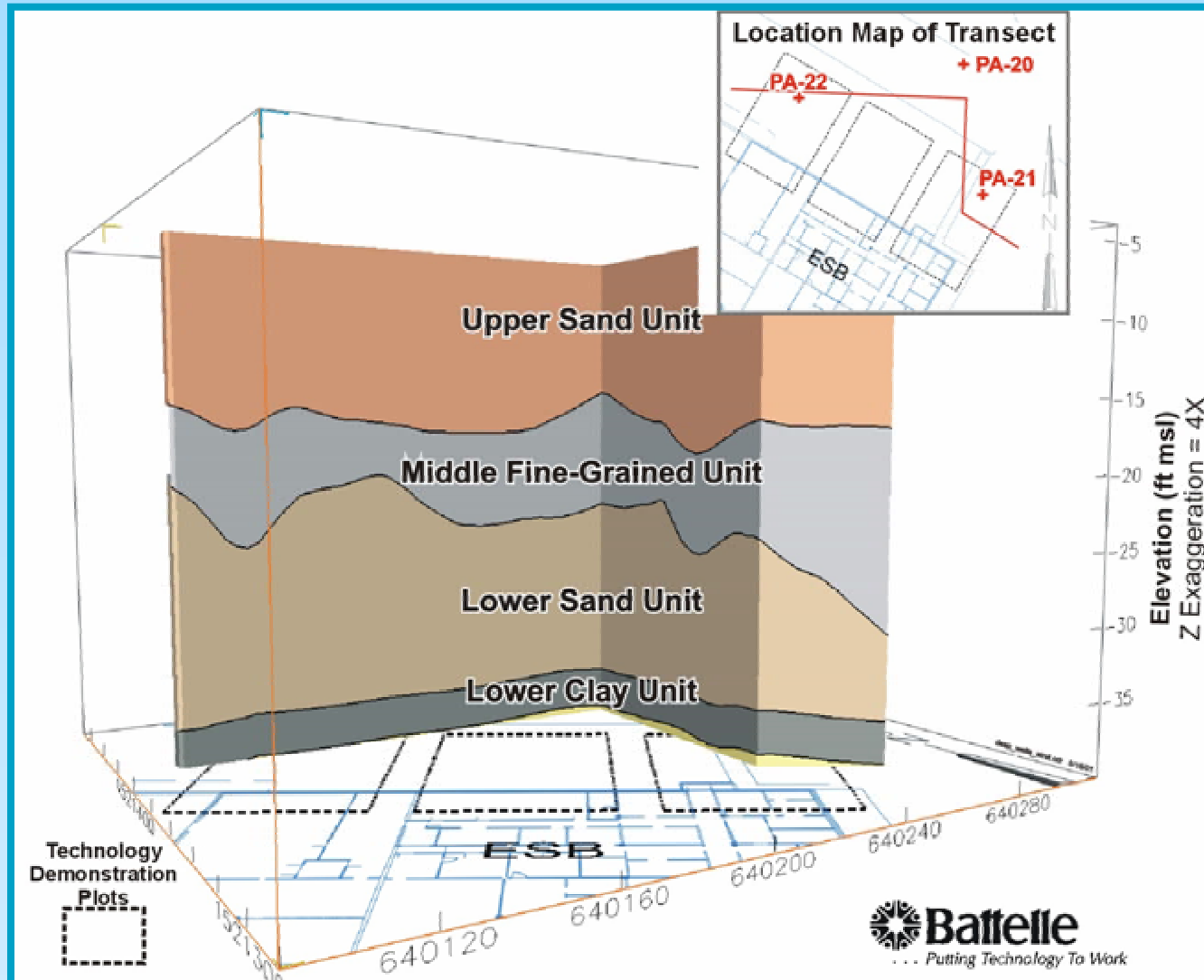
### Using Perimeter Monitoring Wells to Evaluate Potential for TCE/DNAPL Migration

- As confining layer is relatively thin, monitoring wells were required in the confined aquifer below
- Air emission testing is desirable, especially for thermal (e.g., steam injection) or exothermic technologies (e.g., Fenton's reagent)





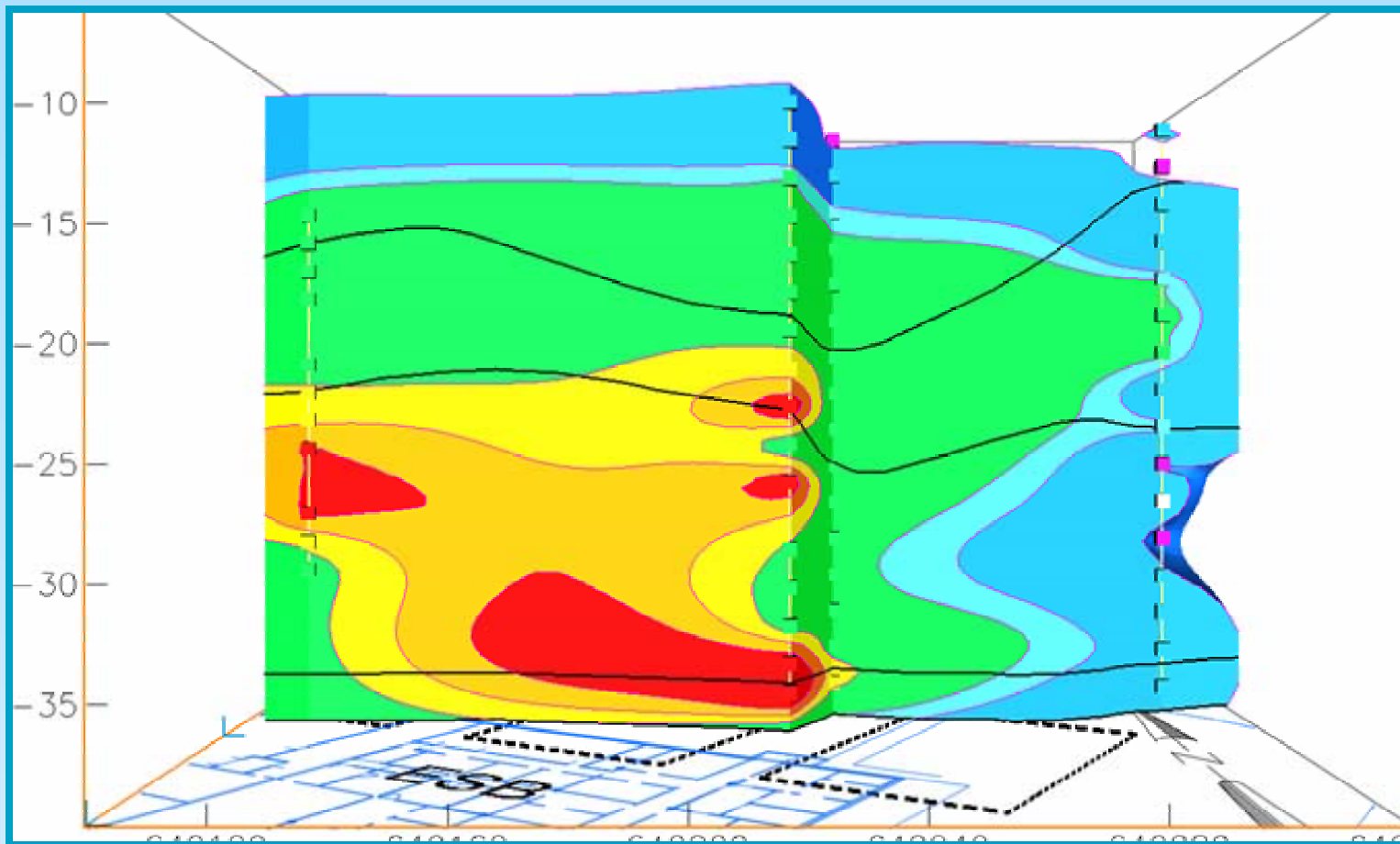
# Site Stratigraphic Cross-Section



# DNAPL (TCE > 300 mg/kg) Source Characterization



*Site characterization indicated DNAPL (yellow and red regions) concentrated near the two low-permeability zones in the surficial aquifer*



# Chemical (Permanganate) Oxidation or ISCO Equipment Layout



Dry  
 $\text{KMnO}_4$   
Hopper

Control Module and  
Liquid Mixing Tank

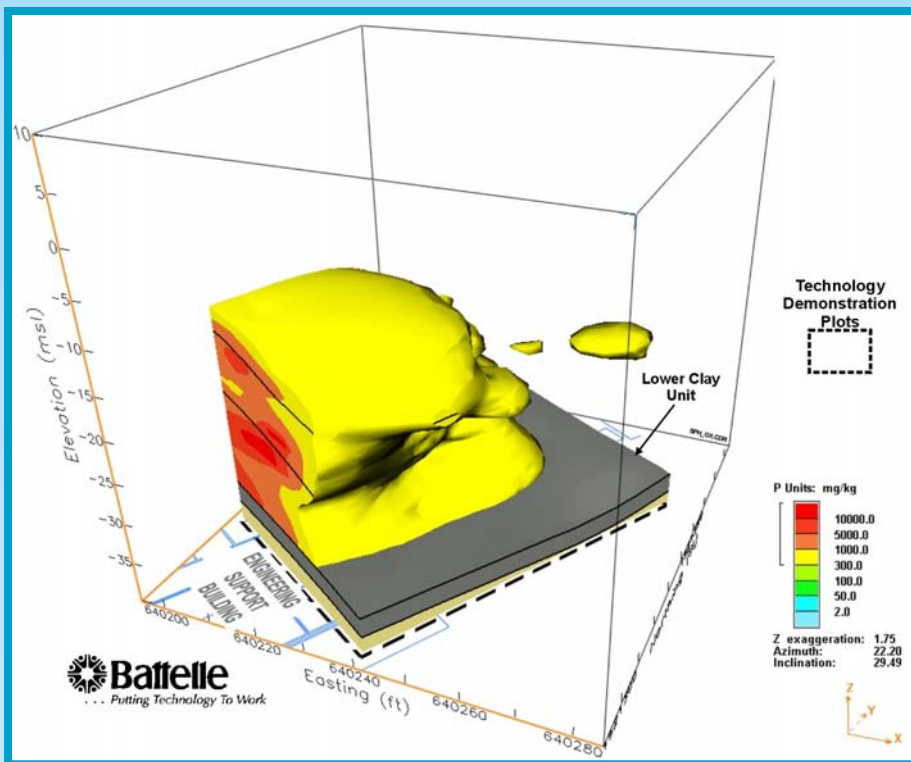
Sand  
Filter  
Tank

Oxidant  
Injection  
Manifold

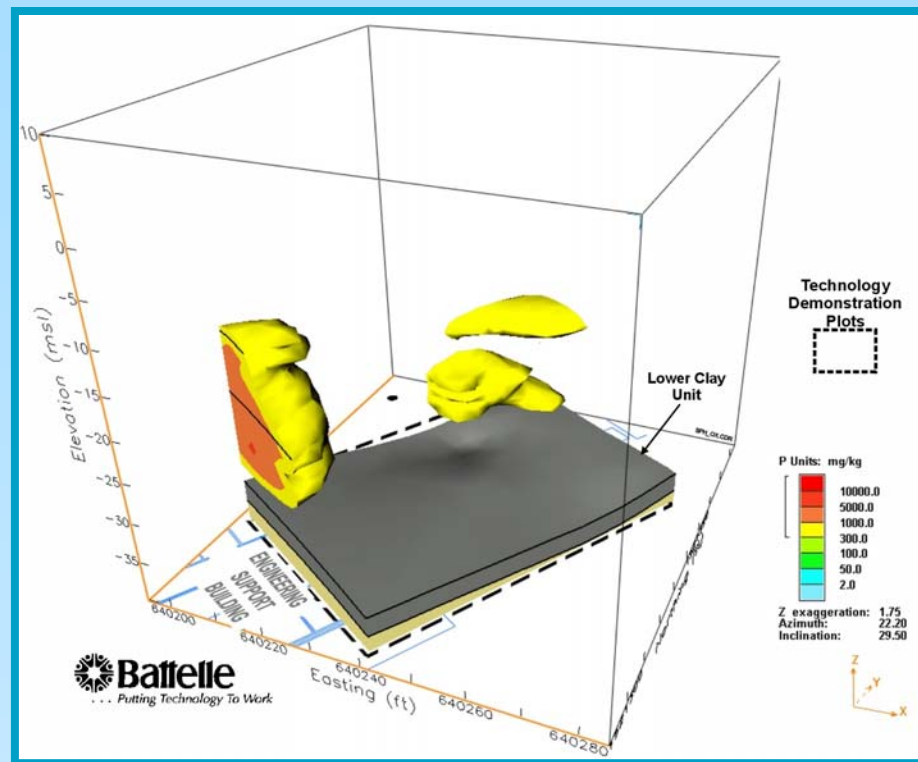


Vendor: IT Corp.

# DNAPL Removal and Oxidant Distribution Efficiency

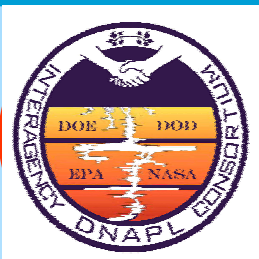


**Pre-Demonstration  
TCE Concentrations in Soil  
in Oxidation Plot**



**Post-Demonstration  
TCE Concentrations in Soil  
in Oxidation Plot**

# TCE Characterization in Test Plots



<b>ISCO</b>	
<b>Pre-Demonstration</b>	
<u>Mass of Total TCE (kg)</u>	
Linear Int.	<b>6,122</b>
Kriging (80% CI)	(6217 to 9182)
<u>Mass of TCE DNAPL (kg)</u>	
Linear Int.	<b>5,039</b>
<b>Post-Demonstration</b>	
<u>Mass of Total TCE (kg)</u>	
Linear Int.	<b>1,100</b>
Kriging (80% CI)	(1511 to 2345)
<u>Mass of TCE DNAPL (kg)</u>	
Linear Int.	<b>810</b>
<u>Change in Total TCE Mass</u>	
Linear Int.	<b>- 82%</b>
Kriging (80% CI)	(-62 to -84)
<u>Change in DNAPL Mass</u>	
Linear Int.	<b>- 84%</b>



# Full Range of TCE Concentrations in Groundwater in the ISCO Plot



ISCO Plot	Pre-demonstration TCE Concentration (mg/L)	Post-demonstration TCE Concentration (mg/L)	Extended Monitoring TCE Concentration (6 months after) (mg/L)
Upper Sand Unit	298 to 1,140	<0.005 to 630	0.019 to 13.3
Middle Fine-Grained Unit	868 to 1,190	<0.005 to 360	0.937 to 356
Lower Sand Unit	752 to 1,160	<b>&lt;0.005 to 220</b>	<b>388 to 436</b>

# Full Range of Chloride Concentrations in Groundwater in the ISCO Plot



ISCO Plot	Pre-demonstration Chloride Concentration (mg/L)	Post-demonstration Chloride Concentration (mg/L)	Extended Monitoring Chloride Concentration (6 months after) (mg/L)
Upper Sand Unit	38 to 53	236 to 237	126 to 531
Middle Fine-Grained Unit	57 to 181	238 to 582	186 to 452
Lower Sand Unit	722 to 752	1,360 to <b>1,730</b>	1,010 to <b>5,070</b>

# Full Range of Aerobic Microbial Counts Analyses in the ISCO Plot



ISCO Plot	Pre-demonstration Aerobic Plate Counts (CFU/g)	Post-demonstration Aerobic Plate Counts (6 months after) (CFU/g)	Extended Monitoring Aerobic Plate Counts (9 months after) (CFU/g)
Upper Sand Unit	1,259 to 100,000	<316 to 7,943	7,943 to 7,943,282
Middle Fine-Grained Unit	501 to 125,893	<316 to 1,584,893	15,849 to 1,258,925
Lower Sand Unit	316 to 316,228	7,943 to 7,943,282	19,952 to 316,228

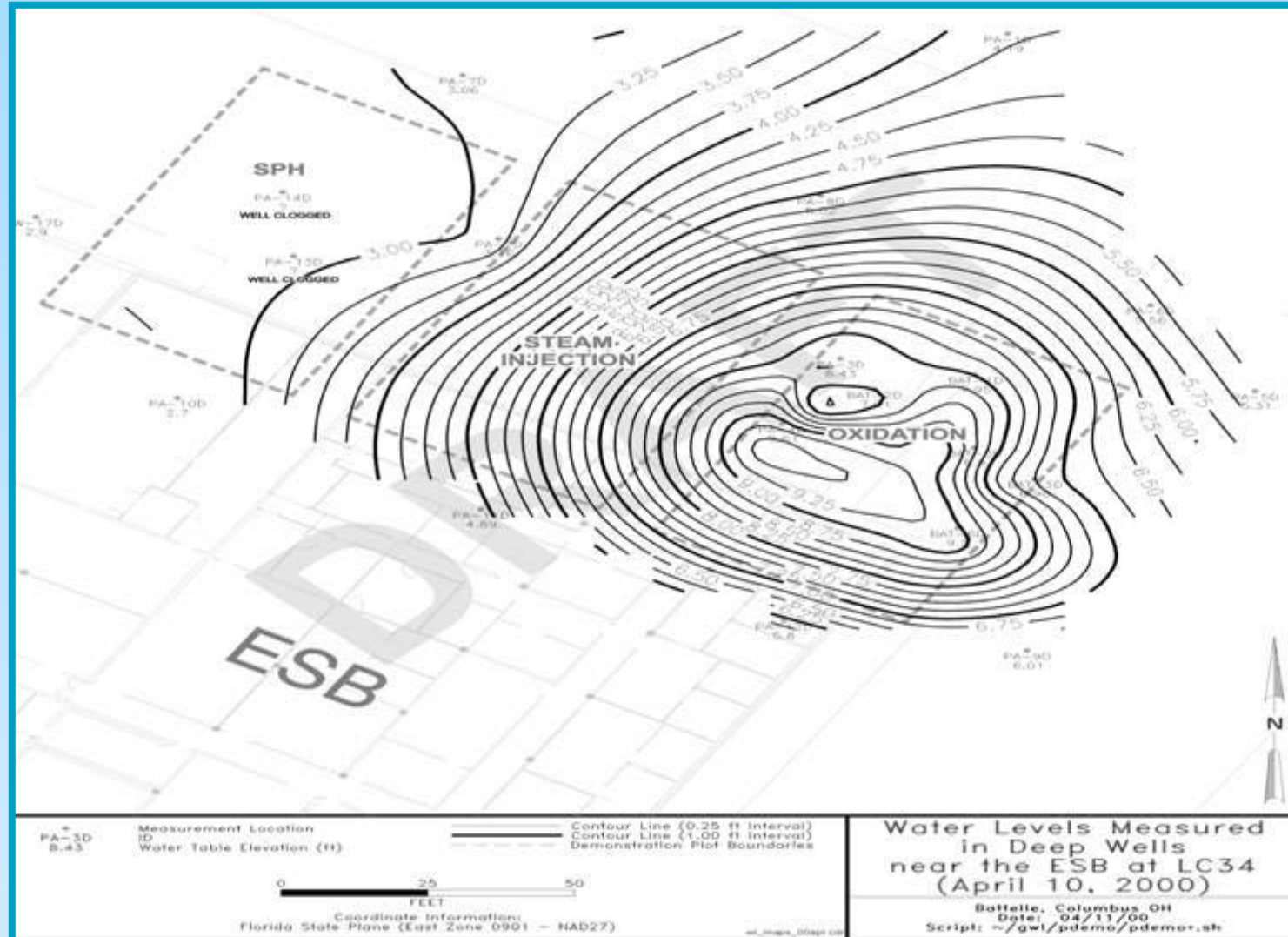


# Full Range of Anaerobic Microbial Counts Analyses in the ISCO Plot



ISCO Plot	Pre-demonstration Anaerobic Viable Counts (cells/g)	Post-demonstration Anaerobic Viable Counts (6 months after) (cells/g)	Extended Monitoring Anaerobic Viable Counts (9 months after) (cells/g)
Upper Sand Unit	2,512 to 316,228	<2 to 6,310	199,526 to 19,952,623
Middle Fine-Grained Unit	794 to 79,433	<2 to 1,584,893	7,943 to 3,162,277
Lower Sand Unit	251 to 63,096	1,259 to >1,585	50,119 to 3,981,071

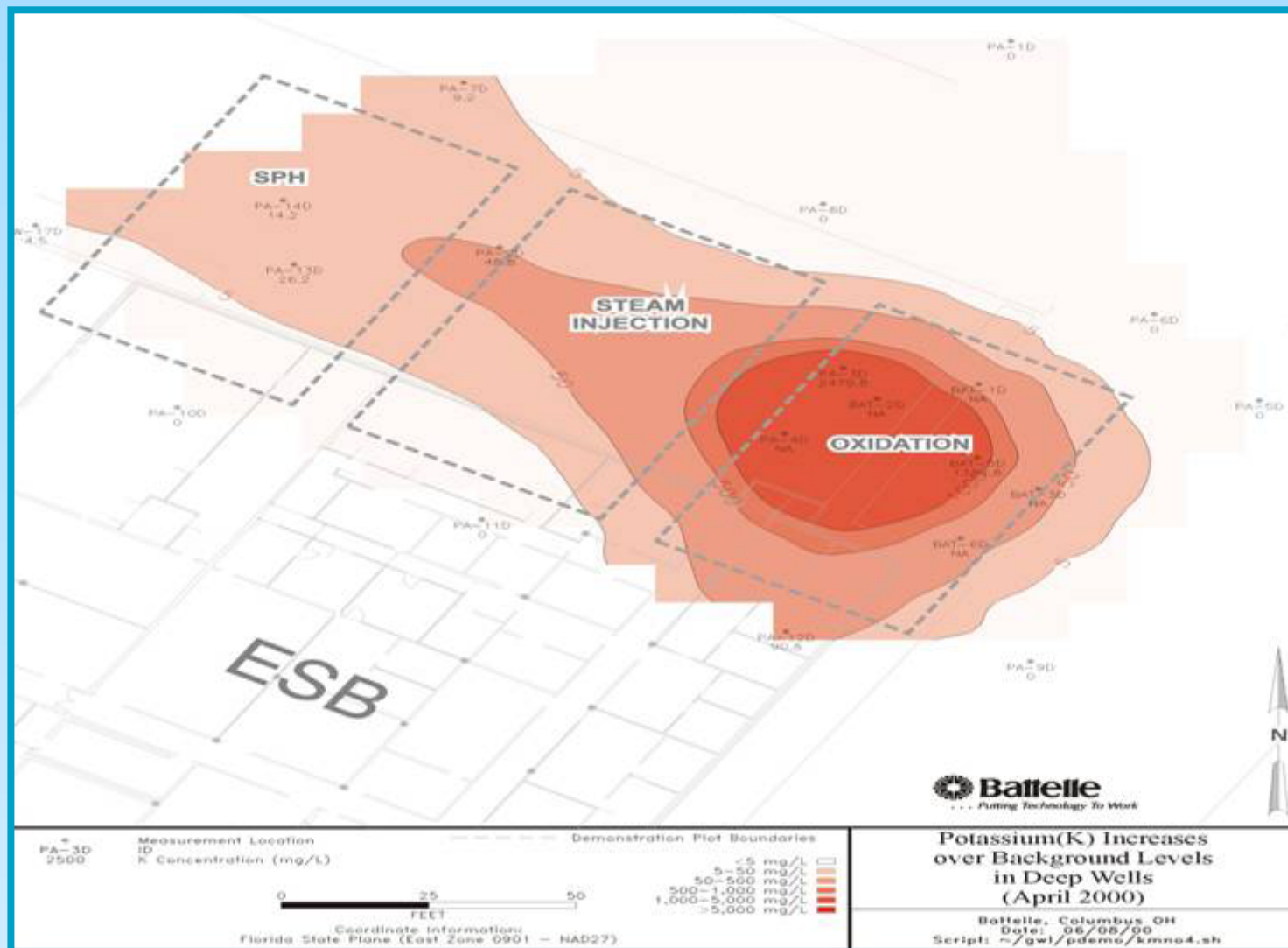
# Oxidation Plot – Hydraulic Gradient during Third Injection



# KMnO<sub>4</sub> Plume at Launch Complex 34



# K Plume at Launch Complex 34



# Changes in Aquifer Properties at Launch Complex 34 due to ISCO



- TCE, DCE decreased in most monitoring wells in test plot
- No significant increase in TCE in surrounding wells or in surrounding soil cores
- pH steady, slight decrease
- ORP increased
- DO steady (low)
- Sulfate increased
- Alkalinity increased
- BOD increased
- TOC increased
- Cr, Ni, Th, and Fe levels increased significantly in the test plot wells; increased to a lesser extent in closely surrounding wells; but no increase in distant (greater than 50 ft away) surrounding wells

# ISCO Costs at Launch Complex 34



Item	Actual Cost
Final design and specifications	\$48,301
Plans and permits	\$23,367
Procurement	\$15,696
Mobilization	\$410,412
Well installation	\$46,675
Pre-Characterization sampling	\$3,292
Tracer test	\$48,846
Phase 1 injection and monitoring	\$124,883
Phase 2 injection and monitoring	\$38,737
Phase 3 injection and monitoring	\$104,566
Process monitoring	\$1,554
Cost reporting	\$24,270
Design/cost modeling	\$9,919
Final technical report	\$49,161
Project management/proposal	\$64,268
<b>Total</b>	<b>\$1,013,947</b>

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# Presumed Advantages and Limitations of Fenton's Reagent



## • Advantages

- Hydroxyl free radical is much more reactive than permanganate and can therefore oxidize many more COCs
- Reactions that generate multiple free radicals destroy nearly all organic contaminants
- Ability to treat strongly sorbed and DNAPL contaminants
- Chemicals involved do not appear to contain trace impurities of concern
- Color is not a concern
- No significant generation of solids that could clog the aquifer

## • Limitations

- Peroxide and hydroxyl free radicals are extremely short-lived and this could limit distribution (reaction rate is diffusion controlled). Other reactive species generated are more long-lived.
- Safety issues with  $H_2O_2$ 
  - ✓ Chemical fires and explosions
  - ✓ Chemical burns
- ✓ Reaction is highly exothermic and higher peroxide concentrations can cause steaming and volatilization of COCs



# Reactivities of Common Organic Contaminants with Hydroxyl Radicals – Second Order Reaction



Compound	$k_{OH\cdot}$ ( $M^{-1} s^{-1}$ )
Benzene	$7.8 \times 10^9$
Toluene	$7.8 \times 10^9$
PCBs	$3 \times 10^9$
PAHs	$1 \times 10^{10}$
2,3,7,8-TCDD (Dioxin)	$3 \times 10^9$
DDT	$3 \times 10^9$
TCE	$4 \times 10^9$
PCE	$2.4 \times 10^9$

# Compounds Not Reactive with Hydroxyl Radicals (OH•)



- **Halogenated Alkanes**

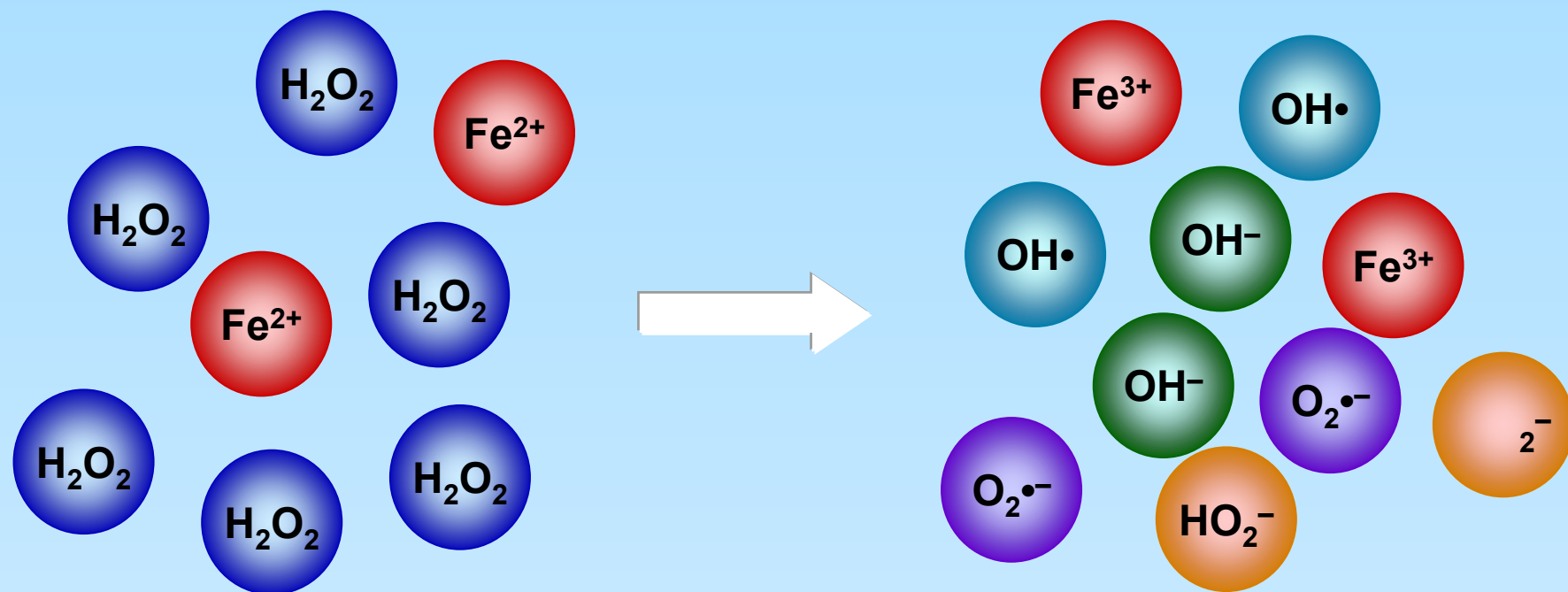
- Carbon tetrachloride
- Hexachloroethane
- Chloroform

# Modified Fenton's Reagent Applications



- Use of relatively high hydrogen peroxide concentrations (2%-12%  $\text{H}_2\text{O}_2$ )
- A range of different materials can catalyze the generation of free hydroxyl and other reactive radicals
  - Soluble Iron (II): Most common so far, with the addition of  $\text{FeSO}_4$
  - Iron (III)
  - Naturally occurring minerals
  - Iron chelates

# Modified Fenton's Reagent: Formation of Other Reactive Species



# Superoxide Anion ( $\text{O}_2^{\bullet-}$ )



## • Characteristics

- Reductant
- Nucleophile
- Relatively long-lived in water
- Very long-lived in organic solvents

## • Compounds Reduced by Superoxide Anion

- Carbon Tetrachloride
- Hexachloroethane
- PCE
- TCE

# Hydroperoxide Anion ( $\text{HO}_2^-$ )



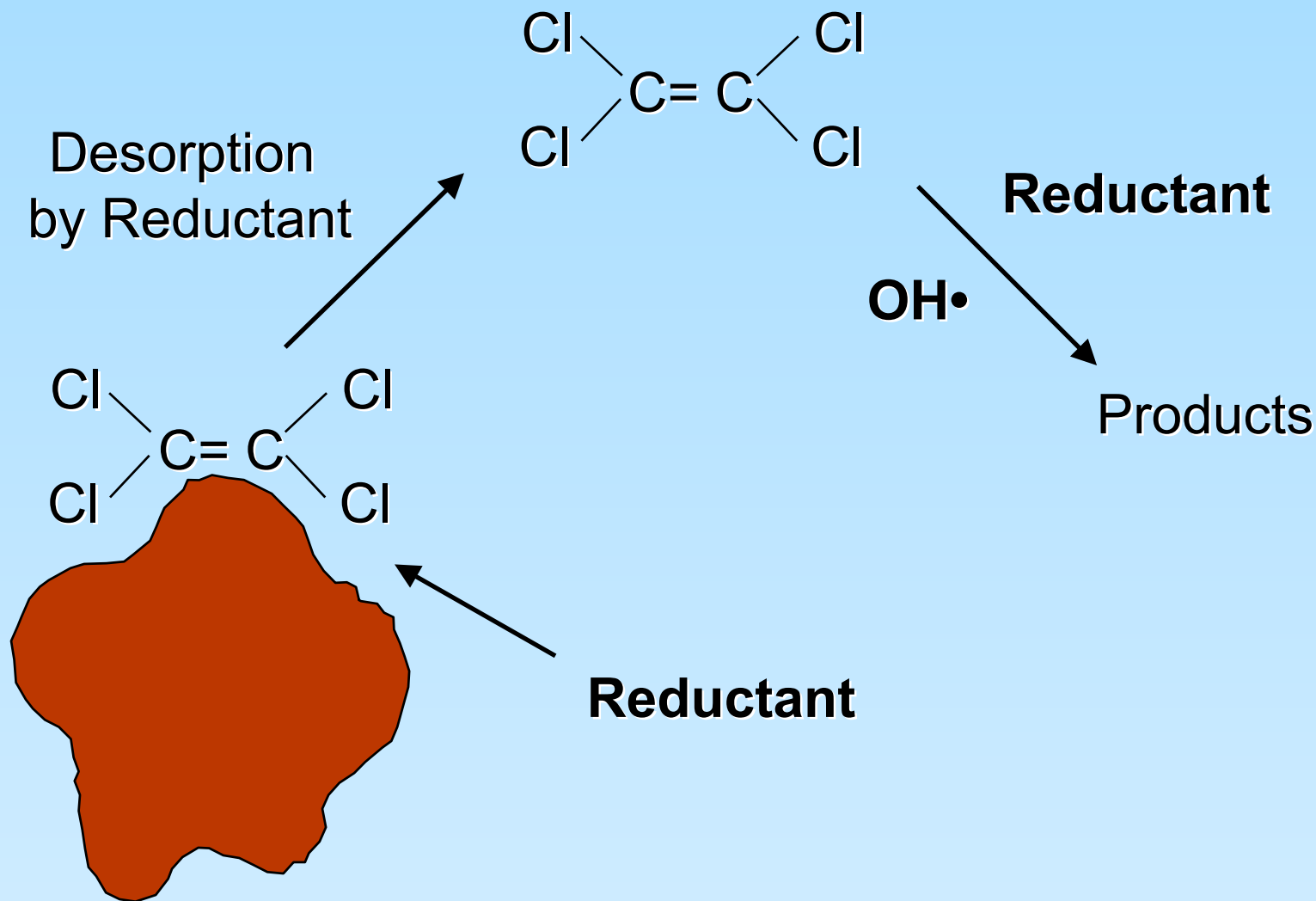
## • Characteristics

- Conjugate base of  $\text{H}_2\text{O}_2$  ( $\text{pK}_a = 11.75$ )
- Reductant
- Strong nucleophile
- Short-lived: recombines with  $\text{H}^+$

## • Compounds Attacked by Hydroperoxide Anion

- 1,3,5-Trinitrobenzene
- Esters
- Amides
- Organophosphorus esters
- Carbamates

# Enhanced Treatment of Sorbed PCE



# Conditions Required in Iron-Catalyzed Fenton's Reactions to Generate Oxygen Transient Species



- Hydroxyl Radicals:  $> 0.01 \text{ mg/L H}_2\text{O}_2$
- Superoxide:  $> 500 \text{ mg/L H}_2\text{O}_2$
- Hydroperoxide:  $> 1\text{-}2\% \text{ H}_2\text{O}_2$
- Implication: Selecting the right concentration of  $\text{H}_2\text{O}_2$  at a given site for a given contaminant (s) is important



# Catalysis by Iron Chelates



- Iron-EDTA (Ethylenediaminetetraacetic Acid)
- Iron-NTA (Nitrilotriacetic Acid)
- Iron-Citrate
- Advantage: Promote Fenton's reactions at neutral pH
- Disadvantages:
  - High potential for metals mobility
  - Chelate is oxidized

# Catalysis by Iron Minerals



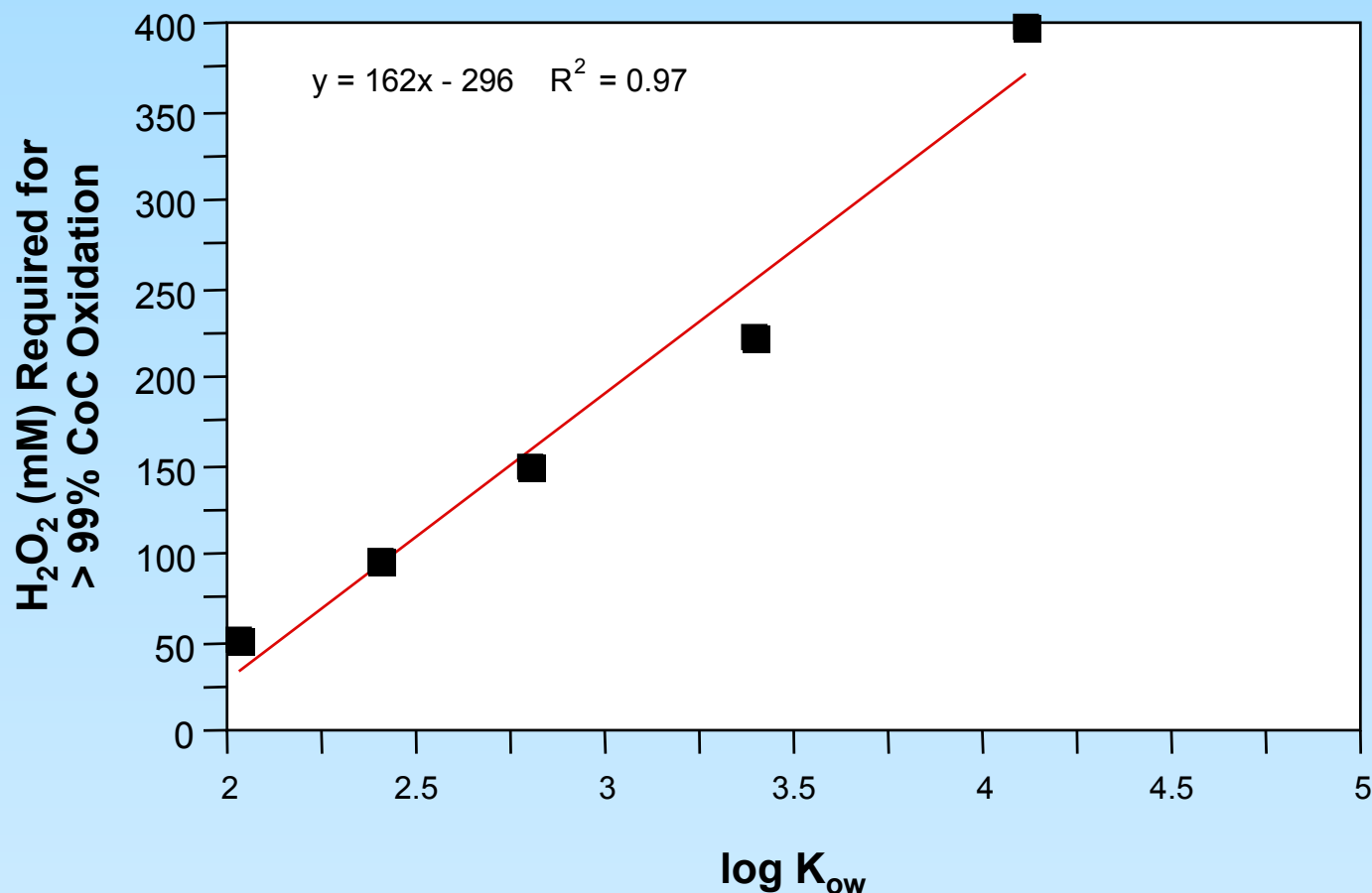
- Natural soil minerals can catalyze the reaction and form reactive radicals
- At many sites, there may not be a need to add ferrous compounds
- pH 3-4 required (acid addition)
- pH rebounds after treatment
- Releases carbonates as  $\text{CO}_2$
- Provides highest degree of  $\text{H}_2\text{O}_2$  stability
- Addition of an iron catalyst not required

# Other Mineral Catalysts



- Different minerals catalyze peroxide decomposition to different radicals
  - Pyrolusite generates  $\text{O}_2^{\bullet-}$
  - Illmenite generates  $\text{OH}^{\bullet}$ ,  $\text{O}_2^{\bullet-}$ ,  $\text{HO}_2^-$
- Implication: Deciding whether or not an added catalyst is required, and if so, which one ( $\text{Fe}^{2+}$ , iron chelate, etc.)
- Implication: Site-specific treatability testing is required at every site to account for the oxidation chemistry in an empirical fashion

# Factors Affecting Fenton's Reagent Application – Nature of the COC determines H<sub>2</sub>O<sub>2</sub> requirements



(From H. Quan, A.L. Teel, R.J. Watts, *J. Hazard. Mater.*, In Press)

# Factors Affecting Fenton's Reagent Application – Presence of COCs as DNAPL



- Evidence from the field has documented DNAPL destruction by Fenton's reagent
- DNAPL destruction by Fenton's reagent has been documented through laboratory research and occurs more rapidly than any other treatment process (up to 50x the rate of natural dissolution)
- DNAPL destruction most likely does not involve hydroxyl radicals, but is likely superoxide
- Even when dissolved COC concentrations do not show a significant decrease, considerable DNAPL mass may have been oxidized
  - Exothermic reaction may cause higher desorption
  - DNAPL destruction may cause improved advective flow and higher dissolved concentrations

- Peroxide instability limits distribution
  - Primary catalysts for the unproductive decomposition of hydrogen peroxide in subsurface are manganese oxides
- Implication: Treatability tests should be conducted to monitor peroxide decomposition rates, and therefore, the well spacing

- Optimum hydrogen peroxide concentrations are usually 0.5%-12% and are highly site specific
  - Lower concentrations (0.5%-1%) are most effective when contaminants are not sorbed and DNAPLS are not present
  - Higher concentrations (2%-12%) are usually required to treat sorbed and DNAPL contaminants
  - Concentrations >12% are ineffective because of highly ineffective exothermic reactions and rapid decomposition of hydrogen peroxide



# Case History – ISCO at MW-13 Area, Industrial Site, California



- Industrial/Undeveloped Area 3 miles from San Francisco Bay
- Solvent Recovery/Distribution Operation from 1972 through 1993
- Currently a Chemical Storage/Distribution Facility Owned by Independent Corporation
- Investigation and Remediation Activities
  - 1995-1999  
Remedial Investigation
  - 1999-2002  
Interim Remedial Actions
  - 2002-  
Final Remedial  
Action Plan/Actions



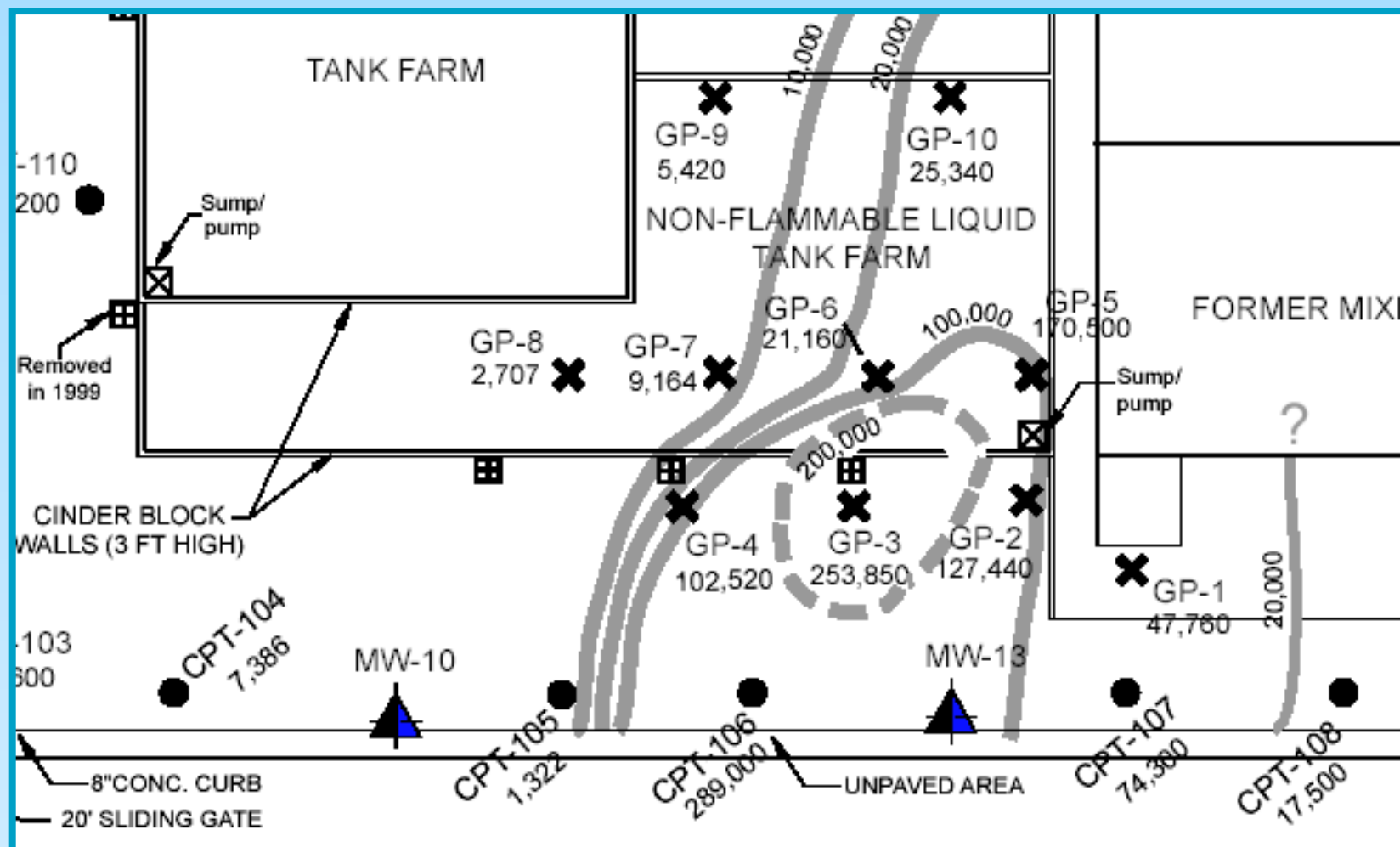
Source: DeHghi et al., 2002

# Case History – ISCO at MW-13 Area, Industrial Site – Hydrogeology

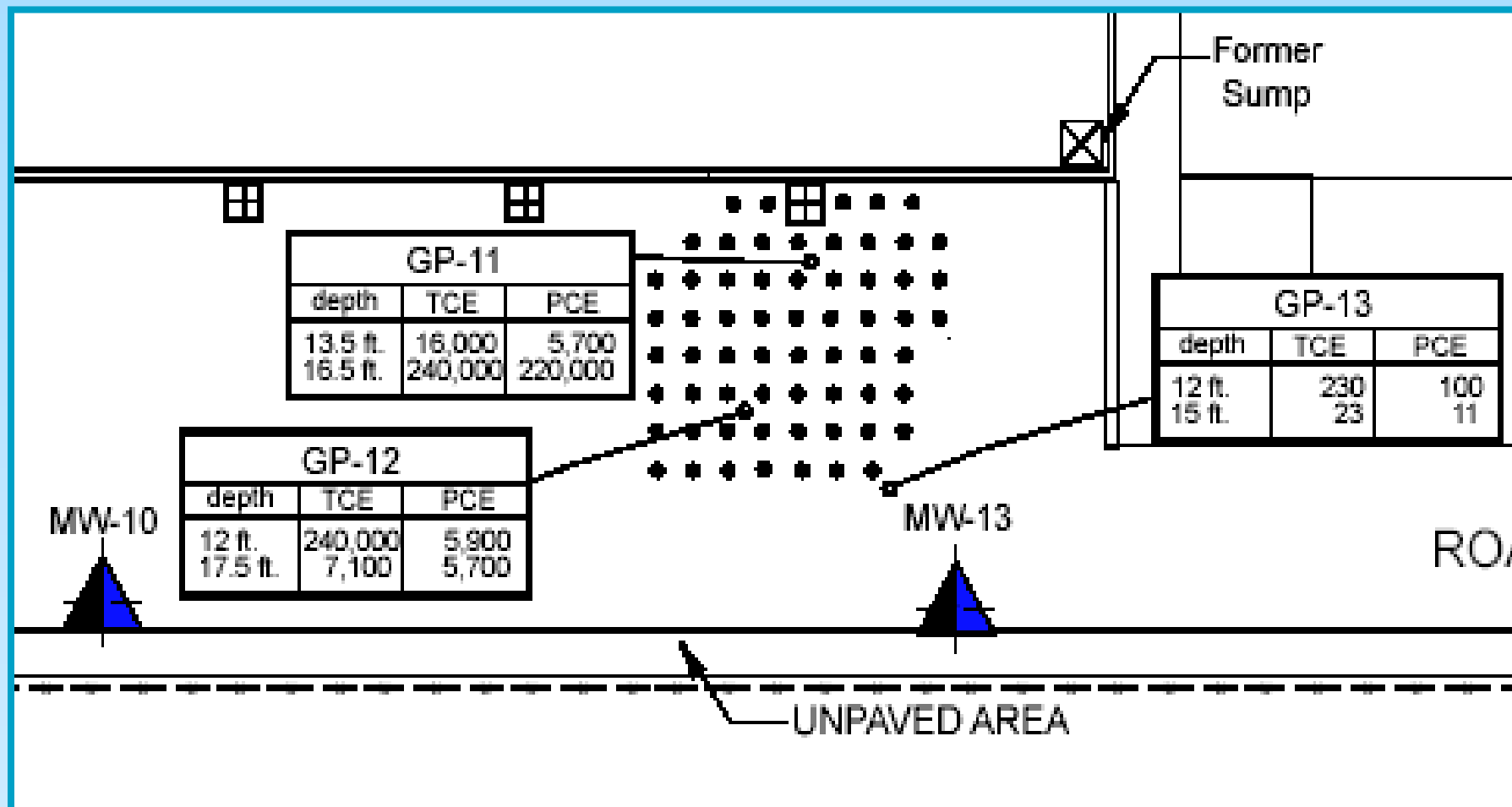


- Pavement and/or fill: 0-2 ft bgs
- Silty clay from base of overlying fill material to 11 to 12 feet bgs
- Static water table at 4 to 6 ft bgs (within Silty Clay)
- Saturated, primarily silty sand from 11 to 12 feet bgs to 18 to 30 feet bgs, referred to as the Shallow Groundwater Zone (SGZ)
- Basal Clay from 18 to 30 feet bgs to 43 to 49 ft bgs
- Groundwater flow velocity in SGZ varies from 41 ft/yr on site to 288 ft/yr downgradient

# Groundwater Plume at MW-13 Area (all concentration units in $\mu\text{g/L}$ )



# Pre-Treatment Soil Sampling (all concentration units in $\mu\text{g}/\text{kg}$ )



# Remedial Action Objectives



- Remove at least 80 percent of COC mass and/or residual DNAPLs in saturated and unsaturated zones
- Mitigate observed trend of increasing COC concentrations in downgradient monitoring well MW-13
- Minimize impact on reductive dechlorination and other natural attenuation mechanisms

## •Objectives

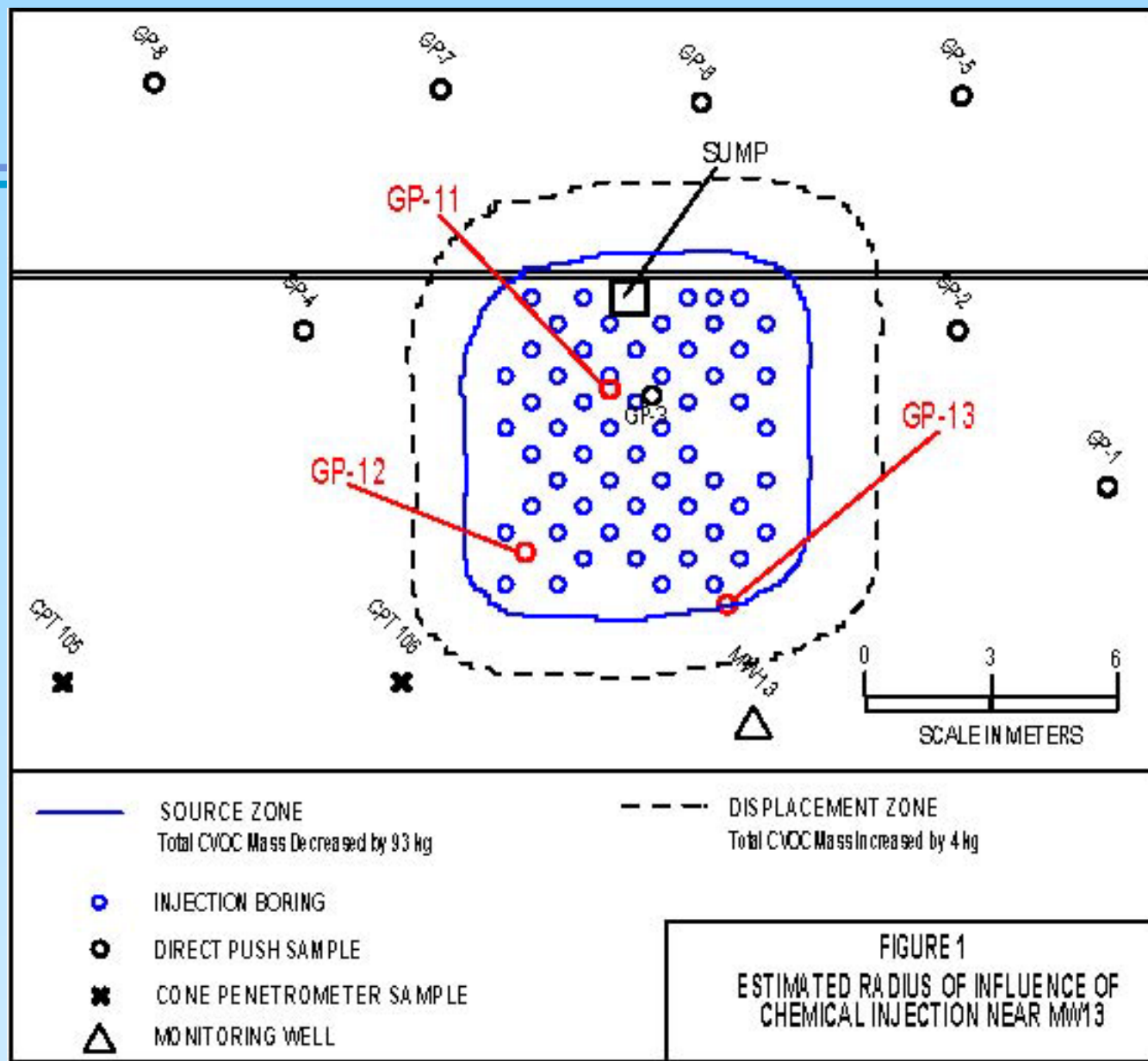
- Determine optimal concentration of  $\text{H}_2\text{O}_2$
- Determine if iron or acid addition is required
- If needed, relative proportion of iron or acid to  $\text{H}_2\text{O}_2$

## •Methods

- Soil and groundwater combined in representative proportions
- Various concentrations of  $\text{H}_2\text{O}_2$ , iron and sulfuric acid
- Effectiveness determined from changes in concentrations of PCE and TCE

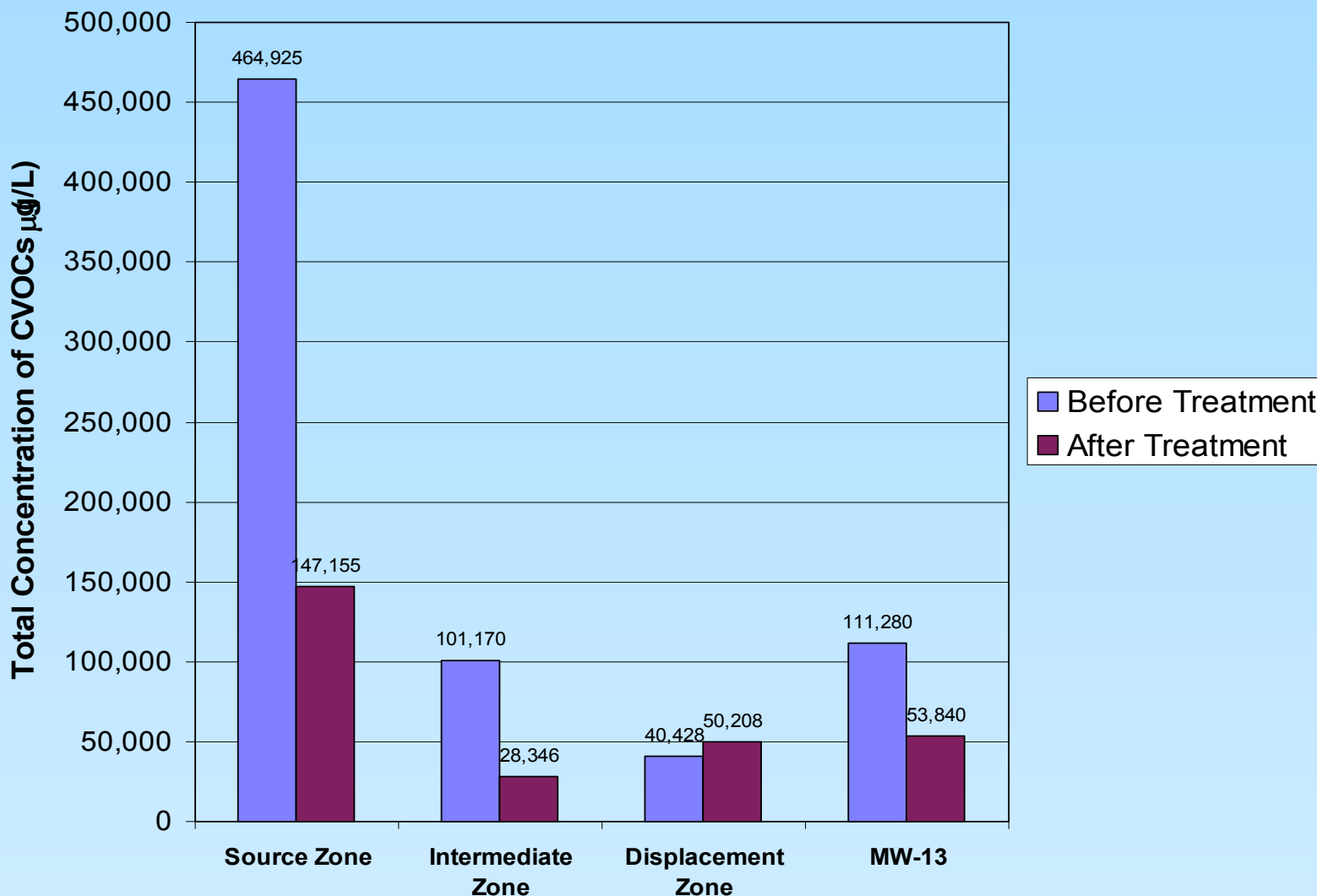
- Injection of iron sulfate was not necessary to catalyze oxidation
- Addition of sulfuric acid to adjust the pH to 3 was necessary to inhibit side reactions
  - Without pH adjustment, carbonate and bicarbonate quench hydroxyl radical before it can degrade VOCs
  - Organic acids not used due to potential side reactions with  $\text{H}_2\text{O}_2$
- The optimal chemical oxidant mixture should be 20 percent hydrogen peroxide, by weight
  - Over 95% decrease in TCE concentration in lab



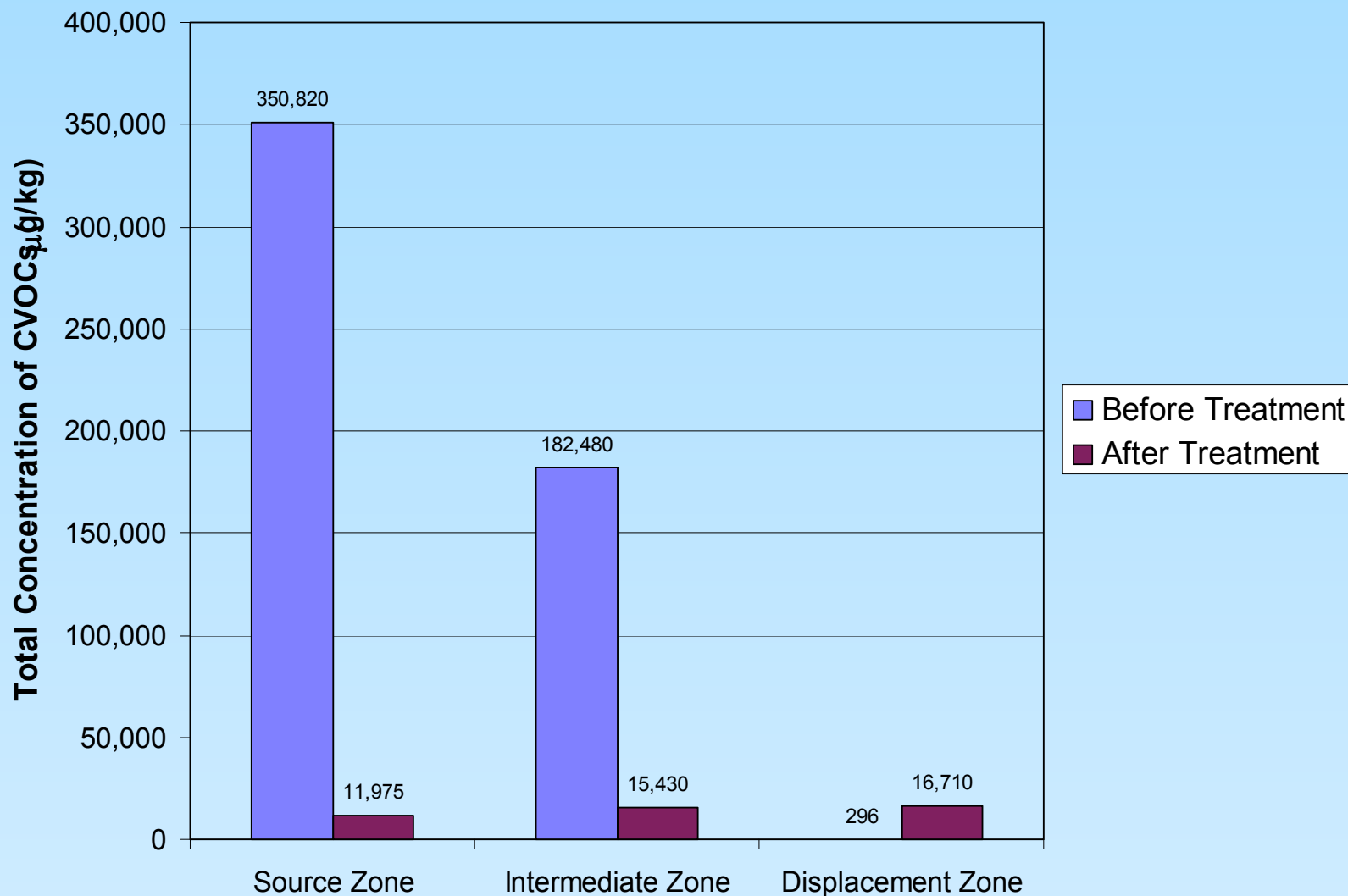


In-Situ Chemical Oxidation of Chlorinated VOCs Using Fenton's Reagent Chemistry and Direct Push Injection in a Shallow, Low Permeability Aquifer

# Performance: Groundwater CVO Concentrations, Short-Term Results



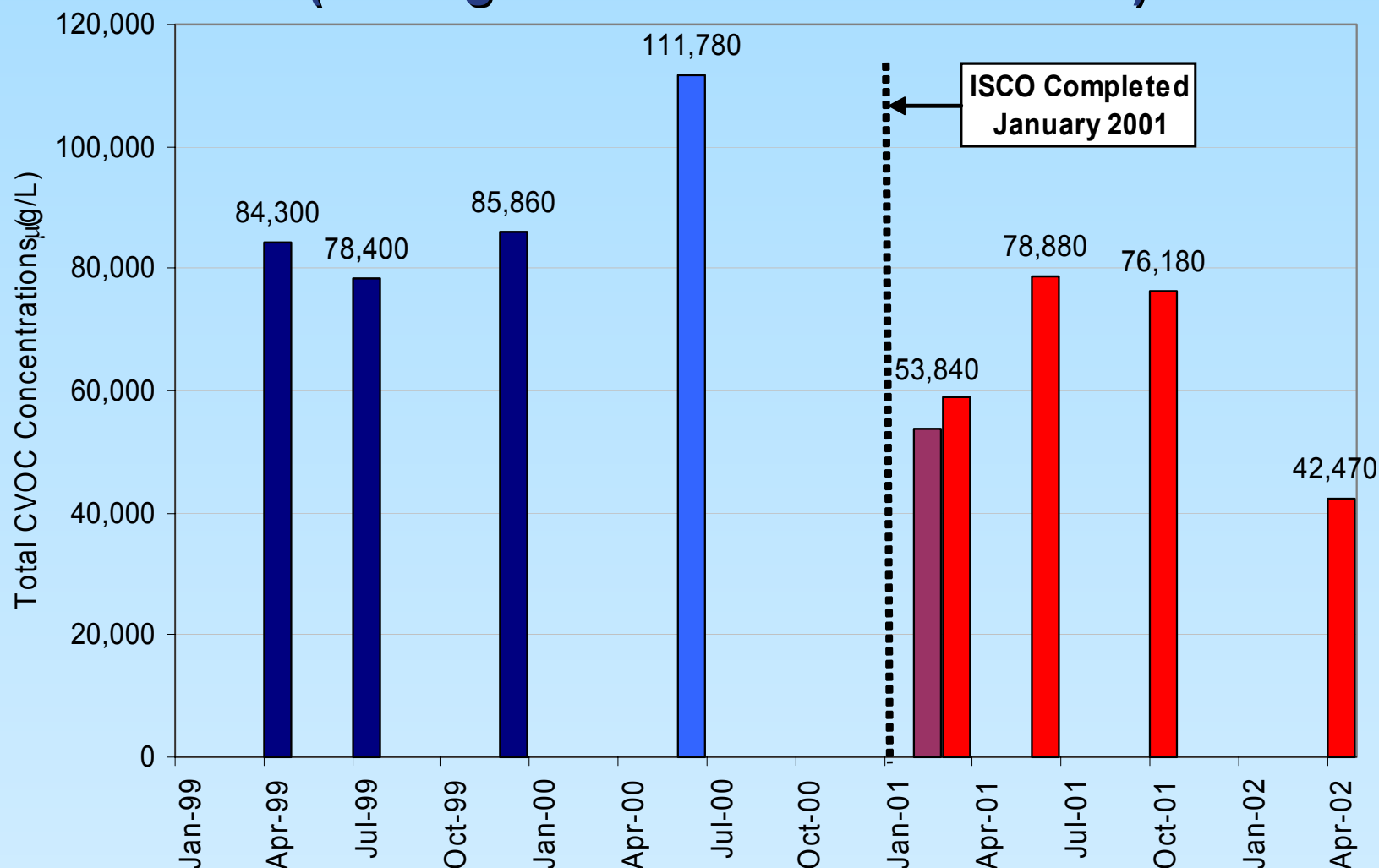
# Performance: Soil CVOC Concentrations, Short-Term Results



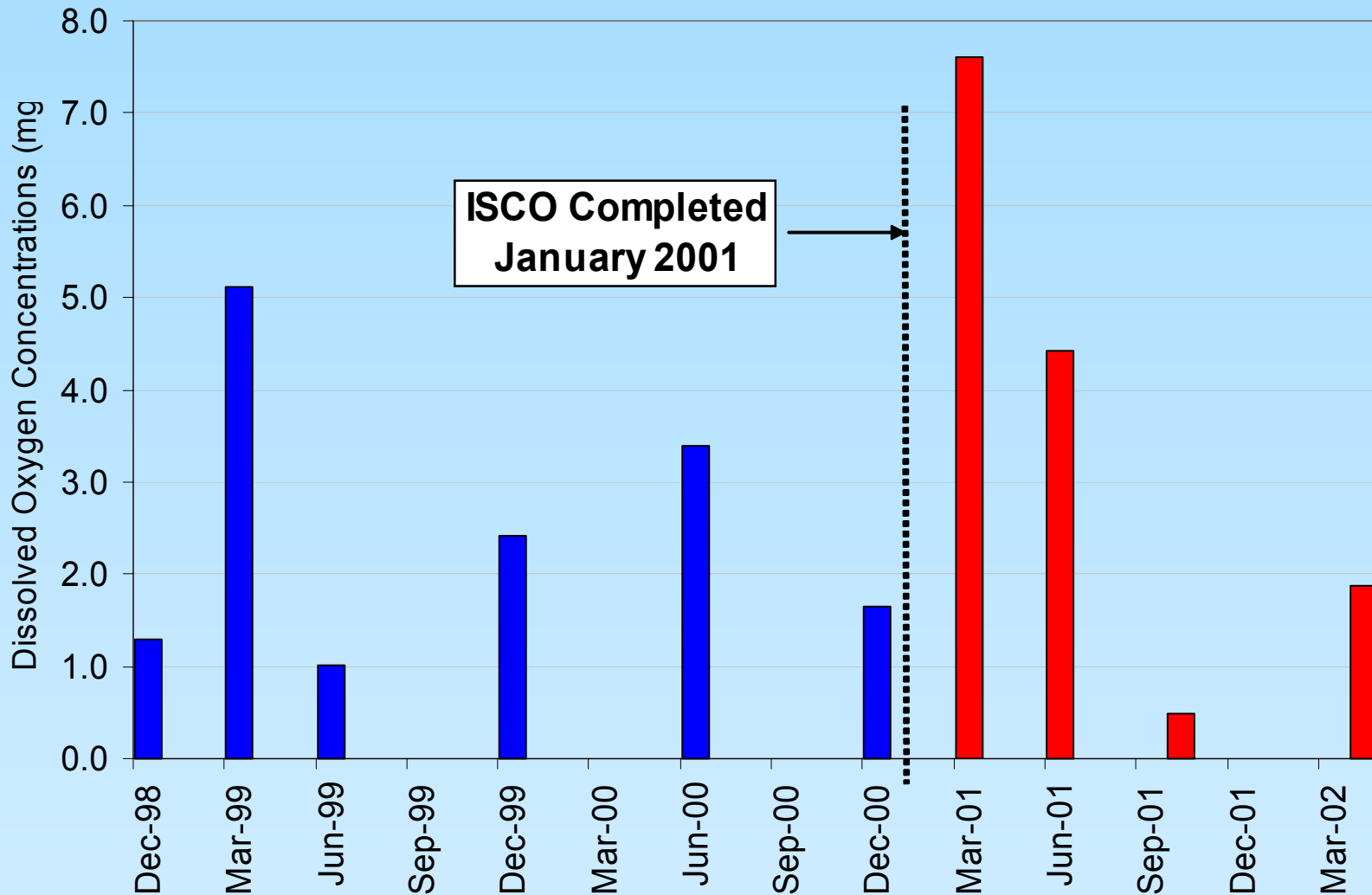
# Long-Term Trends in Groundwater CVOC Concentrations at MW-13



(Downgradient of Treatment Zone)



# Long-Term Dissolved Oxygen Data at MW-13



# pH Data for MW-13 Area



Well	Pre-Treatment		Post-Treatment			
	Dec-99	Jun-00	Mar-01	Jun-01	Oct-01	Mar-02
MW-10	7.2	7.1	7.2	7.1	7.0	6.9
MW-13	7.1	7.2	7.0	7.0	7.0	6.9

DPT Point	Pre-Treatment	Post-Treatment
	Nov-00	Jan-01
Source zone	7.4	7.9
Intermediate	7.9	7.9
Near MW-13	7.6	7.6

# Case Study Summary



- **Achieved more than 85% VOC mass and concentration reduction**
  - Based on pre-treatment and post-treatment direct-push sampling of soil and groundwater
- **VOCs decreased in immediate downgradient well, MW-13**
  - Recent monitoring data shows MW-13 VOC concentrations are stable
- **Long-term monitoring data do not suggest significant VOC concentration rebounding or adverse impact to aquifer chemistry**
- **Short project duration**
  - 2 weeks field treatment, zero O&M, no aboveground waste handling



## •Lessons Learned

- Successful ISCO application hinges on thorough site characterization and respect of hydrogeology and aquifer chemistry
- Success hinges on a good treatability test
- Good monitoring design is essential for measuring success
- ISCO can contribute to overall site cleanup as a source remediation technique to increase effectiveness of downgradient plume remediation

# RI/FS & Remedial Action – Overview



- April 2000: Increasing trend of elevated VOC concentrations in monitoring well MW-13 lead to the discovery of a 5th hot spot area
- Jan 2001: In-Situ Chemical Oxidation (ISCO) implemented at 5th hot spot area
- May 2001: Source Remediation (DPE, ISCO) with groundwater plume MNA recommended as final remedy in Remedial Action Plan

# Presentation Overview



- Introduction
- Advances in Understanding Permanganate Application
  - Oxidation Chemistry and Application
  - Case Study and Cost
- Advances in Understanding Fenton's Reagent Application
  - Oxidation Chemistry and Application
  - Case Study and Cost
- **Conclusions**
  - Permanganate Oxidation
  - Fenton's Reagent
  - Oxidant Selection
  - Regulatory Concerns

# Conclusions: Permanganate Oxidation



- Industrial grade  $\text{NaMnO}_4$  has a lower trace metals content than  $\text{KMnO}_4$  and may be more suitable from a regulatory perspective
- Treatability testing should be done on a site-specific basis to determine optimum oxidant dosage and injection point spacing
- In general, using lower permanganate concentrations is better than using higher concentrations. Between 0.1 to 3% permanganate concentrations have been effectively used in the past.
- At many sites, SOD is much higher than the COC demand. SOD may drive oxidant dosage – permanganate concentration and injection time – as also the well spacing.

# Conclusions: Permanganate Oxidation (cont.)



- Precautions should be taken when using strong permanganate, but **handling** hazards are not as great as for  $\text{H}_2\text{O}_2$ .
- Cheaper to buy  $\text{KMnO}_4$  as a solid, but may be worthwhile obtaining a solution.
- **Distributing** the oxidant to the COC is the biggest challenge. Pilot injection using a single well or drive point can be useful.
- Many vendors do a tracer test to determine radius of influence and well spacing required at a site. Generally, 5-foot, 10-foot, or sometimes 15-foot injection point spacing is required
- Permanganate **persists in the environment** for a much longer time and can therefore diffuse into tighter pores or other regions around the injection point, even if these regions cannot be reached through advection.
- The lag time between injection events may have to be longer than with Fenton's for the most efficient use.

# Conclusions: Permanganate Oxidation (cont.)



- **Regulatory** approval may be necessary if trace metals are anticipated to exceed groundwater standards temporarily
- Reduction/increase in dissolved CoC concentrations may not be a good **indicator** of how much DNAPL mass has been oxidized
- Increase in chloride could perhaps be a better indicator

# Conclusions: Fenton's Reagent Oxidation



- **Treatability and pilot-scale studies are almost always required for system design**
- **Process conditions that should be evaluated include**  
[1] Different catalysts: soluble iron, naturally occurring minerals, iron chelates; [2] pH: 3-4 and neutral, and  
[3] Peroxide concentrations: 0.5%-12%
- **The primary design consideration affecting injection well placement is hydrogen peroxide stability**

# Conclusions: Fenton's Reagent Oxidation (cont.)



- Fenton's process generates not only hydroxyl radicals, but also other oxygen radicals (Superoxide anion, Hydroperoxide)
  - Other oxygen radicals, such as superoxide, are more long-lived and required for successful remediation
  - The mix of radicals provides a matrix of oxidants, reductants, and nucleophiles that can degrade almost all organic contaminants
  - The generation of superoxide can cause increased desorption and subsequent oxidation of contaminants
  - Fenton's chemistry is not simple; treatability tests (empirical evidence) are required on a site-specific basis



- **30%-50% Hydrogen peroxide solutions can cause severe skin burns**
- **Hydrogen peroxide is unstable. It is decomposed by transition metals, metal oxides, light, high pH.**
- **Potential for fires and explosions**

- **Permanganate Preferred**

- Where target COCs are amenable to oxidation by permanganate
- In tighter soils, where diffusion is likely to be the major mechanism for oxidant distribution
- Where soil has a strong pH buffering capacity

- **Fenton's Reagent (or Modified Fenton's Reagent) Preferred**

- Where target COCs are not amenable to oxidation by  $\text{KMnO}_4$
- In sandy soils, where advection is the major mechanism of distribution

# Oxidant Selection (cont.)



- **Other Oxidants**

- Hydrogen peroxide
- Ozone
- Persulfate + Permanganate

- **Possible Permit Requirements**

- Underground injection code (UIC) permit waiver to inject oxidant

- **Process Chemistry Concerns Among Regulators**

- Acid addition (Fenton's)
- Metals release
- Degradation products (e.g., dichloroacetic acid)

# **Subsequent Biodegradation of COC Residuals**

## **- Regulatory and economic issue for the site**



- **Oxidant injection does not kill all the microorganisms. Surviving organisms can reestablish colonies.**
- **Surprisingly, TOC, BOD, and COD of the groundwater has actually increased following oxidation (complex organic matter is oxidized to simpler molecules that are more soluble and bioavailable). Therefore, a renewed carbon source is available for the surviving microbes.**
- **Many aquifers have sufficient buffering capacity against any persistent changes in pH, ORP, and DO**
- **At many sites, microbial populations have rebounded in the months following oxidation treatment**

# Points of Contact



- **Naval Facilities Engineering Service Center**

- (805) 982-1660

- **Battelle**

- (614) 424-3403

- [battelle.org](http://battelle.org)

- **Washington State University**

- (509) 335-3761

## • Books and Reports

- Battelle, 2002. *Demonstration of ISCO Treatment of a DNAPL Source Zone at Launch Complex 34 in Cape Canaveral Air Station*. Final Innovative Technology Evaluation Report. Prepared for the Interagency DNAPL Consortium by Battelle, Columbus, Ohio.
- Siegrist, R., M. Urynowicz, O. West, M. Crimi, and K. Lowe. 2001, *Principles and Practices of In-Situ Chemical Oxidation Using Permanganate*. Battelle Press, Columbus, Ohio. ISBN 1-57477-102-7.

## • Journal Papers and Conference Publications

- DeHghi, B., A. Hodges, and T. Feng. 2002. Post-treatment evaluation of Fenton's Reagent in-situ chemical oxidation. In *Remediation of Chlorinated and Recalcitrant compounds – 2002*. Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, May 2002. Battelle Press, Columbus, Ohio. ISBN 1-57477-132-9.
- Marvin, B., J. Chambers, A. Leavitt, and C. Schreier. 2002. Chemical and engineering challenges to in-situ permanganate remediation. In *Remediation of Chlorinated and Recalcitrant compounds – 2002*. Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, May 2002. Battelle Press, Columbus, Ohio. ISBN 1-57477-132-9.
- Pignatello, J.J., and Baehr, K., 1994. Waste management: ferric complexes as catalysts for "Fenton" degradation of 2,4-D and metalochlor in soil. *J. Environ. Qual.* 23:365-369.

## •Journal Papers and Conference Publications (Cont.)

- Watts, R.J., M.D. Udell and R.M. Monsen. 1993. Use of iron minerals in optimizing the peroxide treatment of contaminated soils. *Water Environ. Res.* 69:839-845.
- Watts, R.J. 1998. *Hazardous Wastes: Sources, Pathways, Receptors*. John Wiley & Sons. New York. 764 p.
- Watts, R.J., B.C. Bottenberg, M.E. Jensen, T.H. Hess, and A.L. Teel. 1999. Role of reductants in the enhanced desorption and transformation of chloroaliphatic compounds by modified Fenton's reactions. *Environ. Sci. Technol.* 33:3432-3437.

## •Web Sites

- Fenton's Reagent: Subsurface Contaminants Focus Area (DOE/EM-0484) <http://apps.em.doe.gov/OST/pubs/itsrs/itsr2161.pdf>
- Effect of Fenton's Reagent on Aquifer Geochemistry and Microbiology at the A/M Area, Savannah River Site (DOE) <http://www.osti.gov/servlets/purl/755213-cpabOq/webviewable/755213.pdf>